

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 November 2002 (21.11.2002)

PCT

(10) International Publication Number
WO 02/093664 A2

(51) International Patent Classification⁷: H01L 51/30

(21) International Application Number: PCT/IT02/00301

(22) International Filing Date: 7 May 2002 (07.05.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
MI92001A 000995 15 May 2001 (15.05.2001) US

(71) Applicant (for all designated States except US): SAES
GETTERS S.P.A. [IT/IT]; Viale Italia, 77, I-20020 Lainate
(IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): BOFFITO, Claudio
[IT/IT]; Via Papa Giovanni XXIII, 2, I-20017 Rho (IT).
TOIA, Luca [IT/IT]; Via della Fontana, 14/A, I-21040
Carnago (IT). CATTANEO, Lorena [IT/IT]; Via Prato 3,
I-21052 Busto Arsizio (IT).

(74) Agents: ADORNO, Silvano et al.; Società Italiana
Brevetti S.p.A., Via Carducci, 8, I-20123 Milano (IT).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

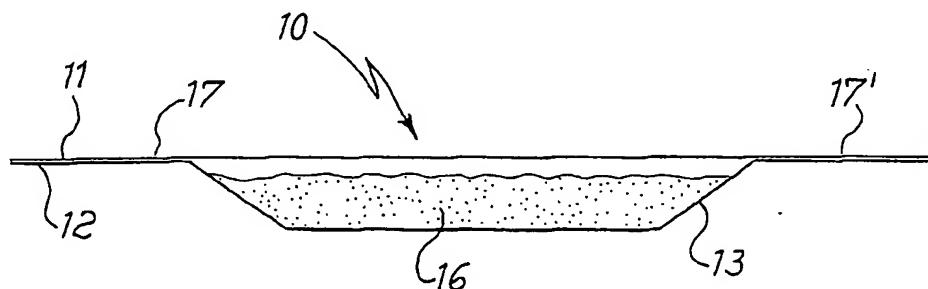
(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: CESIUM DISPENSERS AND PROCESS FOR THE USE THEREOF



(57) Abstract: Cesium dispensers based on the use of a mixture between a reducing agent and a cesium compound selected among molibdate, tungstate, niobate, tantalate, silicate and zirconate are described. Some processes for the use of these dispensers are also described.

WO 02/093664 A2

"CESIUM DISPENSERS AND PROCESS FOR THE USE THEREOF"

The present invention relates to cesium dispensers and a process for using
5 them.

Cesium has been used for a long time in the electronic field. In particular this metal has been used in the past for the production of photosensible surfaces, for example of image intensifiers or photomultiplier tubes.

A novel application field for cesium is in the OLED (Organic Light
10 Emitting Display) screens.

In short, an OLED is formed of a first transparent planar support (of glass or plastics); a second, not necessarily transparent support that may be realized in glass, metal or plastics, essentially planar and parallel to the first support and secured along the perimeter thereof, so as to form a closed space; and a structure
15 in said space that is active in forming an image. The active structure is formed in turn by a first set of linear and reciprocally parallel, transparent electrodes, deposited on the first support; a multilayer of different electroluminescent organic materials comprising at least one layer of electron-conductive material and one layer of an electronic vacancies (also defined in the field as "holes") conductive
20 material deposited on the first set of electrodes; a second set of linear and reciprocally parallel electrodes that are orthogonally oriented with respect to those of the first set and in contact with the opposite side of the multilayer of organic materials, so that the latter is comprised between the two sets of electrodes. For a more detailed description of the structure and operation of OLED screens one can
25 refer for instance to patent applications EP-A-845924, EP-A-949696, JP-A-9-078058 and patent US 6,013,384. Recently it has been ascertained that the doping of one or more layers of the organic multilayer with little amounts of electron-donor metals, in particular cesium, enables to reduce the potential difference to be applied to the sets of electrodes for the functioning of screens, and thus the energy
30 consumption of the latter.

Due to its high reactivity to atmospheric gases and moisture, cesium is not

usually used in industry as pure metal, but rather in the form of its compounds stable to air at room temperature.

Some cesium compounds release the metal by simple heating. Among these compounds, alloys with silicon or germanium may be cited as described for
5 example in patent application EP-A-360317 and patent US 5,066,888 as well as the intercalation compound of cesium with graphite, having formula CsC_8 , cited in patent application EP-A-130803. These compounds have however no practical application at industrial level.

Cesium dichromate, $\text{Cs}_2\text{Cr}_2\text{O}_7$, or more commonly cesium chromate,
10 Cs_2CrO_4 are normally used in the industry in mixture with a reducing agent. By heating these mixtures at temperatures generally over 500 °C, and usually between 550 and 650 °C, a reaction takes place wherein chromium is reduced to a lower valence as a consequence of which cesium is released in vapor form. As
reducing agents aluminum, silicon or getter alloys, i.e. alloys based on titanium or
15 zirconium with aluminum or one or more transition elements, are generally used. The use of these mixtures is described for example in patent US 2,117,735.

These compounds are generally introduced into suitable dispensers that are able to retain solid particles of the compounds, but have at least a portion of the surface permeable to cesium vapors. Various forms of dispensers are the object
20 for instance of patents US 3,578,834, US 3,579,459, US 3,598,384, US 3,636,302, US 3,663,121 and US 4,233,936. A further property required for cesium dispensers is not to release gases that are detrimental to the operation of devices wherein cesium is used during their production.

Cesium chromate and dichromate suffer however the disadvantage of
25 containing hexavalent chromium, that may cause irritations by contact, ingestion or inspiration and may be carcinogenic in case of protracted exposures.

In production processes of common devices in which cesium is used (image intensifiers or photomultipliers) high temperatures are reached, and only by using chromate and dichromate one can avoid the release of cesium in an early stage of
30 the process. In addition, in these cases limited productions are obtained and consequently the amounts of chromate that are used are limited too.

The temperatures of production processes of OLEDs are on the contrary lower, and for these screens productions on very large scale are foreseen, in the order of tens of millions of pieces per year. With these production volumes, the safety problems linked with the transportation and use of chromates become
5 outstanding. In the production of OLEDs it is thus possible and highly desirable not to resort to the use of Cs_2CrO_4 or $\text{Cs}_2\text{Cr}_2\text{O}_7$ to evaporate cesium.

The object of the present invention is to provide cesium dispensers particularly suitable for the production of OLED screens, wherein cesium is not present in the form of a chromium salt.

10 A further object of this invention is to provide a process for the use of cesium dispensers in the production of OLED screens.

These objects are achieved by the present invention, which in a first respect relates to cesium dispensers formed by a container able to retain solid particles but having at least a part of the surface permeable to cesium vapors and containing a
15 mixture of at least a cesium compound and at least a reducing agent, characterized in that the cesium compound is selected among molybdate, tungstate, niobate, tantalate, silicate and zirconate.

The invention will be described below with reference to the drawings in which:

20 - Figure 1 shows, in a perspective view, a first possible cesium dispenser according to the invention;

- Figure 2 shows a sectional view along line II-II' in Fig. 1 of the same dispenser;

25 - Figure 3 shows a perspective, partially cut-away view of another possible dispenser of the invention;

- Figure 4 shows a top plan view of a further possible dispenser of the invention; and

- Figure 5 shows a sectional view along line V-V' of the dispenser in Fig. 4.

The inventors have found that mixtures of one or more reducing agents and
30 one or more compounds selected among cesium molybdate, Cs_2MoO_4 , cesium tungstate, Cs_2WO_4 , cesium niobate, CsNbO_3 , cesium tantalate, CsTaO_3 , cesium

silicate, Cs_2SiO_3 and cesium zirconate, Cs_2ZrO_3 , are compatible with the production process of OLEDs, in that they are able to evaporate cesium at lower temperatures than the corresponding chromates without practically releasing gases potentially harmful for OLEDs, mainly comprising water vapor. In particular the
5 evaporation temperatures of cesium from these mixtures are generally lower than 450°C ; these temperatures can easily be locally reached on the cesium dispenser in the purification chambers of OLEDs.

The mixtures used in the dispensers of the invention may comprise more than one cesium compound and more than one reducing element or compound,
10 but generally a single component per each kind is used.

As a reducing agent it is possible to use one of the already known components used in dispensers based on chromates, such as aluminum, silicon, zirconium or titanium, or alloys containing zirconium or titanium, such as for example the alloy having percent composition by weight Zr 84% - Al 16%,
15 produced and sold by the Applicant under the trade name St 101[®], or the alloy having percent composition by weight Zr 76,5% - Fe 23,5%, produced and sold by the Applicant under the trade name St 198[®].

In order to promote the contact between cesium compound and reducing agent, these are preferably used in the form of powders. Both components of the
20 mixture have generally a particle size lower than 1 mm, preferably lower than 500 μm ; even more preferably the particle size is comprised between about 10 and 125 μm . Powders with grains smaller than 10 μm are generally difficult to be treated in production and retained in the dispenser; furthermore, in case of the reducing agent, powders too fine may become pyrophoric, thus causing safety problems in
25 the production plant. On the contrary, with powders having sizes higher than those named, the contact between the mixture components get worse, and the reaction causing the release of cesium slows down.

The weight ratio between cesium compound and reducing agent can vary between wide limits. Said ratio is preferably comprised between 10:1 and 1:10.
30 The use of cesium compound in great excess with respect to the reducing agent does not offer practical advantages; on the contrary, mainly when the reducing

agent is a getter alloy, such as the named alloy St 101[®], its excess in the mixture may become useful since the portion not involved in the reaction with cesium compound can carry out an absorbing action on the gases that may get free during the reaction.

5 The mixture can be used in the form of free powders, or it is possible to preform pellets of the same; the use of pellets bears the advantage of further improving the contact between the components of the mixture, and facilitating the charging operations of the container.

10 The container can be realized in every material and shape compatible with the specific application.

15 In particular, with reference to the material, this must be chemically inert with respect to the working atmosphere and cesium releasing mixture in the whole temperature range foreseen for the use, generally between the room temperature and about 450 °C; in the same temperature range, the material forming the container must not undergo noticeable physical changes, such as to modify its mechanical resistance or shape, and must have the lowest possible values of gas emission. Materials having these properties are for instance metals or metallic alloys, ceramics, graphite and boron nitride, BN. The use of metals is preferred due to their easier workability and formability. A further advantage in using
20 metals, graphite and BN is that the dispenser can be heated up to the cesium evaporation temperature by simple passing of current through the container walls. Preferred metals and alloys for manufacturing the container are molybdenum, tantalum, tungsten, nickel, steel and nickel-chromium alloys.

25 The shape of the container may be any of those known from the previously named patents US 3,578,834, US 3,579,459, US 3,598,384, US 3,636,302, US 3,663,121 and US 4,233,936. Containers of various shapes and materials are also available on sale, for example from the Austrian company Plansee or from the USA company Midwest Tungsten Service.

30 In figures 1 and 2 is represented, in perspective and sectional views respectively, a possible dispenser using the mixtures of the invention; in particular figure 2 shows the sectional view of the dispenser along line II-II' of figure 1.

Dispenser 10 is formed of two metal foils 11 and 12. A depression 13, obtained for instance by cold forming the foil is arranged in the central part of foil 12. Foil 11 has, in its central zone 14 (bordered by the broken line in figure 1), a set of small through holes 15. In the assembled dispenser, zone 14 corresponds to
5 depression 13; the latter contains a mixture 16 of at least one cesium compound and at least one reducing agent according to the invention. Foils 11 and 12 can be secured to each other, outside depression 13, in any way assuring powders tightness; for example, a mechanical fixing can be obtained in the form of
10 "tongues" in a foil folded on the other, or a fixing by continuous or spotted welding, or combinations of these methods. Finally, dispenser 10 has two lateral projections 17 and 17' useful for the handling with mechanical means in the production line and for connection to electric terminals in order to heat it.

In figure 3 another possible dispenser 30 according to the invention is represented partially cut away. In this case the container of mixture 16 is formed
15 by a foil 31 (for instance metallic) similar to foil 12 of figures 1 and 2, whereas the surface portion of the container permeable to cesium vapors is formed by a porous body 32 comprising or formed of a getter material. Body 32 can be maintained in position by any method; for example only, in figure 3 a retaining element 33 is shown secured to foil 31 by means of welding spots 34; body 32 can
20 be maintained in the desired position by means of any other retaining element, fixed to foil 31 in any suitable way. Body 32 may be formed of sintered getter material only; such a getter body can be obtained for example according to the method described in patent EP-B-719609 in the name of the Applicant. Alternatively, body 32 may be formed of getter material deposited according to
25 various methods on a supporting open structure, such as for instance a wire net having meshes of suitable dimensions; similar open structures are described for example in patent US 4,146,497 in the name of the Applicant, or may be produced by depositing getter particles on a wire net through the electrophoretic technique, as described for example in patent US 4,628,198. By this structure, the getter
30 body 32 fulfils the double service of allowing the passage of cesium vapors yet retaining the particles of mixture 16, and avoiding the pollution of the atmosphere

in the process chamber, where the dispenser is used, by gases such as water, carbon oxides, etc. that can be released by the components of said mixture.

Finally, figures 4 and 5 represent a further possible form of dispenser using the mixtures of the invention, that is useful when is necessary to evaporate little amounts of cesium; this dispenser has the structure described in patent US 3,598,384. Figure 4 shows the dispenser in a top plan view, and figure 5 shows a sectional view along line V-V' of figure 4. Dispenser 40 is formed of a container 41 having an extended structure with a trapezoidal section and a longitudinal slit 42 blocked by a wire 43 that allows the evaporation of cesium but prevents the powdery mixture 44 from escaping; container 41 is tapered at its ends about two terminals 45, 45' that fulfill the double service of closing said ends and as electric terminals for heating the assembly.

In a second aspect, the invention relates to a process for using the above-described dispensers in the production of screens of OLED sort.

The structure of an OLED (briefly described above) is produced, by means of techniques that are typical in the microelectronic industry, by prearranging the first transparent support and depositing in sequence thereon the various forming layers. The electrodes are generally deposited according to techniques such as the screen printing; the layers of organic materials are obtained in general by means of evaporation or the technique known as "spin coating", consisting in the deposition of a drop of liquid material on the support and swift rotation of the latter.

As the used organic materials and especially the second set of electrodes (generally made of metals such as barium) are extremely sensitive to the atmospheric agents and in particular to water vapor, at least the arranging steps of these layers and the subsequent ones must take place in proper chambers, under vacuum or inert atmosphere. The cesium dispensers of the invention are especially suitable for introducing the element into the active structure during these treatments in the chamber.

In particular the process of the invention comprises the steps of:

- introducing a cesium dispenser into a chamber having a controlled

atmosphere and being provided with means for heating it;

- arranging in said chamber the production intermediate of OLED screen as obtained after having formed the organic multilayer;

- causing the evaporation of cesium from the dispenser by heating the latter;

5 and

- carrying out the subsequent production phases of the OLED screen up to its sealing with the second support.

For the objects of the invention, it is not required that these phases are carried out in the above order; in addition, the cesium evaporation operation may
10 be accomplished in different production times of the OLED. Possible changes in the process of the invention will be described below in more detail.

The chamber with controlled atmosphere can be one of those already provided for carrying out the other production process steps of the OLEDs, or can be a chamber dedicated to the cesium evaporation operation. This chamber must
15 be provided with means for heating the dispenser, that can be radiative (infrared lamps) or, in the case of a dispenser with metallic or graphitic container, of inductive type; the heating can alternatively be carried out by direct passage of current, by prearranging a heatable support for the dispenser or even, in the case of containers in graphite, boron nitride and metal (for instance of the type
20 previously described with reference to figures 1 and 2), by heating the dispenser through direct passage of current in the container walls; in this latter case the heating means in the chamber will be simply electric through means with suitable terminals for connection to the container.

In the case where the cesium evaporation chamber is a chamber in which
25 also other process operations are effected, the dispenser will be introduced prior to the evaporation phase and thermally activated at a convenient time. If on the contrary the chamber is used exclusively for evaporating cesium, in the chamber where the dispenser is already present there is introduced a production intermediate of the OLED. Cesium is then evaporated from the dispenser by
30 heating it with the previously named means at a temperature between about 250 and 450 °C, according to the specific cesium compound used therein.

The evaporation of cesium can be effected in various intermediate production phases of the OLED. For example, the production of OLED may comprise the following main operations:

- production of the first set of electrodes on the first transparent support;
- 5 - production of the organic multilayer on the first set of electrodes;
- evaporation of cesium on the organic multilayer;
- production of the second set of electrodes on the organic multilayer;
- other possible operations and sealing along the perimeters of the first and second supports.

10 Alternatively, the cesium evaporation operation can be subsequent to the production of the second set of electrodes.

The invention will be further illustrated in the following examples relating to some cesium compounds of the invention, and in particular the molibdate and tungstate, in addition to a comparison example with the chromate of the prior art.

15 **EXAMPLE 1**

A cesium dispenser is produced, wherein as a compound of said element the molibdate, Cs_2MoO_4 , is used.

The dispenser is of the kind described in the specification with reference to figures 4 and 5. Container, wire and terminals are made in nickel-chromium alloy.
20 The portion filled with the mixture has a section of about 1 mm x 1,5 mm and a length of 25 mm. This container is filled with a mixture of one part by weight of cesium molibdate in powder form and five parts by weight of the named St 101[®] alloy; the powders have a particle size between 10 and 125 μm . The linear charging of the container is of about 40 mg of mixture per centimeter.

25 The so produced dispenser is sample 1.

EXAMPLE 2

A cesium dispenser as described in example 1 is produced, by using however as cesium compound the tungstate Cs_2WO_4 . This dispenser is sample 2.

(COMPARATIVE) EXAMPLE 3

30 A cesium dispenser as described in example 1 is produced for comparison, by using as cesium compound the chromate Cs_2CrO_4 . This dispenser is sample 3.

EXAMPLE 4

This example relates to the cesium evaporation tests from the dispensers produced in the previous examples.

Samples 1-3 are assembled within a chamber that is then evacuated, are
5 connected to electric loops and fed by a current generator. The current is gradually increased with a slope of 0.1 A/min. The temperature of the sample is measured by a thermocouple welded on the outer wall of the container, and the current value is registered that produces the start of cesium evaporation, taken by the aid of a triode sensor mounted near the evaporation slit. The thus taken temperature values
10 of evaporation start are given in the following table.

Cs compound	Temperature of evaporation start (°C)
Cs ₂ MoO ₄ (invention)	295
Cs ₂ WO ₄ (invention)	250
Cs ₂ CrO ₄ (comparison)	625

Based on the test results, it stands out that mixtures using the compounds of the invention are able to release cesium vapors in current, and thus temperature,
15 conditions that are lower with respect to cesium chromate.

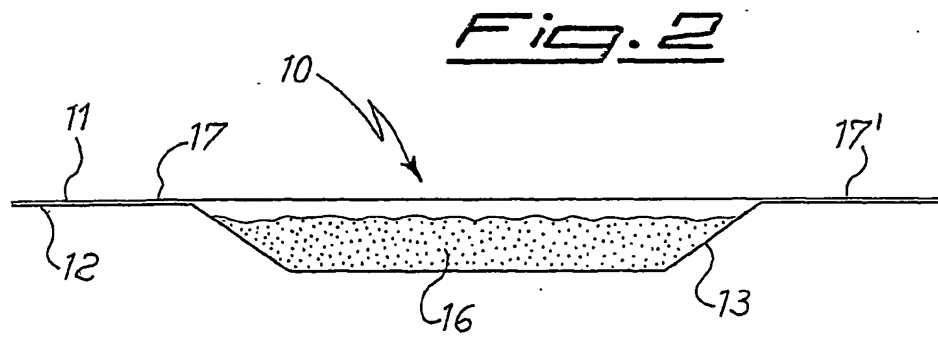
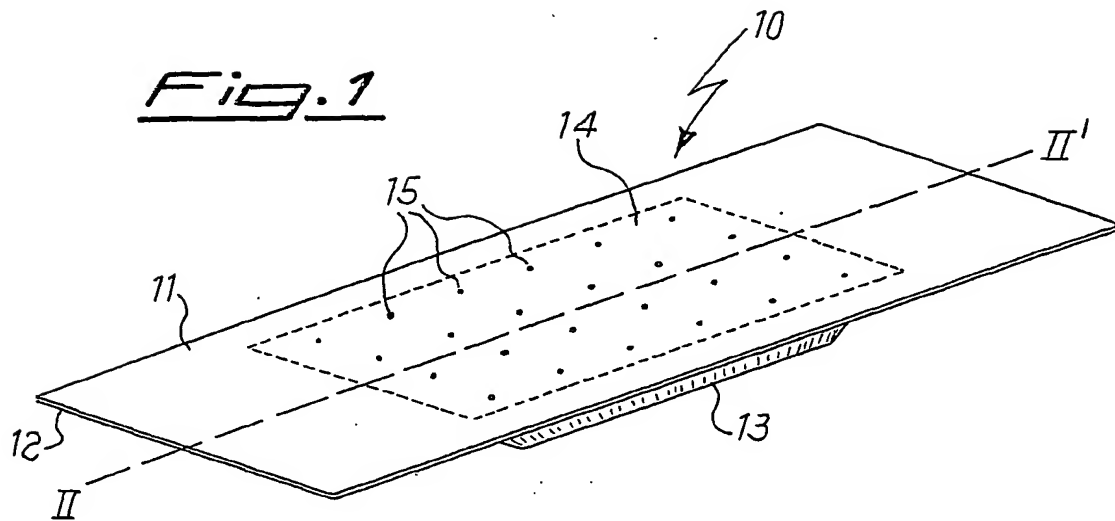
CLAIMS

1. Cesium dispenser (10; 30; 40) formed of a container capable of retaining solid particles, but having at least a portion (14; 32; 42) of the surface permeable to cesium vapors and containing a mixture (16; 44) of at least one cesium compound and at least one reducing agent, characterized in that the cesium compound is selected among molybdate, tungstate, niobate, tantalate, silicate and zirconate.
2. A dispenser according to claim 1, wherein said mixture comprises a single cesium compound and a single reducing agent.
3. A dispenser according to claim 1, wherein the reducing agent is selected among aluminum, silicon, zirconium, titanium or alloys containing zirconium or titanium.
4. A dispenser according to claim 3, wherein the reducing agent is an alloy having a percent composition by weight Zr 84% - Al 16%.
5. A dispenser according to claim 3, wherein the reducing agent is an alloy having a percent composition by weight Zr 76,5% - Fe 23,5%.
6. A dispenser according to claim 1, wherein the materials forming said mixture are in powder form.
7. A dispenser according to claim 6, wherein said powders have a particle size lower than 1 mm.
8. A dispenser according to claim 7, wherein said powders have a particle size lower than 500 μm .
9. A dispenser according to claim 8, wherein said powders have a particle size between 10 and 125 μm .
10. A dispenser according to claim 1, wherein the weight ratio between the materials forming said mixture is from 10:1 to 1:10.
11. A dispenser according to claim 1, wherein the container is made of a material selected among metals, metal alloys, graphite, boron nitride and ceramics.
12. A dispenser according to claim 11, wherein said material is selected among molybdenum, tantalum, tungsten, steel and nickel-chromium alloys.
13. A cesium dispenser (10) according to claim 1, composed by a container formed by joining two metal foils (11, 12), the first foil (11) having in its central zone (14) a plurality of holes (15) of small size and the second foil (12) having in its

corresponding central zone a depression (13); a mixture (16) of at least one cesium compound and at least one reducing agent in said depression; the junction between said two foils being made so as not to allow solid particles from escaping; and said dispenser having two lateral extensions (17, 17') for the handling with mechanical means and the connection to electric terminals of the dispenser itself.

14. A cesium dispenser (30) according to claim 1, composed by a container formed of a foil (31) in a depression of which is contained a mixture (16) of at least one cesium compound and at least one reducing agent, and of a porous body (32) comprising or formed of getter material, maintained in position on said depression by means of a retaining element (33) secured on said foil by welding spots (34).
15. A cesium dispenser (40) according to claim 1, composed by a container (41) having extended structure with trapezoidal section and an longitudinal slit (42) blocked by a wire (43) that allows the evaporation of cesium but prevents the mixture of powders (44) present in the container from escaping, said container being tapered at the ends around two terminals (45, 45') that close said ends and form electric contacts for heating the dispenser.
16. A process for the use of cesium dispensers according to one of the previous claims in the production of screens of OLED type formed of a first transparent support, a first set of electrodes, an organic multilayer, a second set of electrodes and a second support, comprising the steps of:
 - introducing a cesium dispenser in a chamber with controlled atmosphere and provided with means for heating the same;
 - arranging in said chamber a production intermediate of the OLED screen as obtained after having formed the organic multilayer;
 - causing the evaporation of cesium from the dispenser by heating the latter; and
 - carrying out the subsequent production steps of the OLED screen up to its sealing with the second support.
17. A process for the use of cesium dispensers according to claim 16, comprising the following series of operations:

- production of the first set of electrodes on the first transparent support;
 - production of the organic multilayer on the first set of electrodes;
 - evaporation of cesium on the organic multilayer;
 - production of the second set of electrodes on the organic multilayer;
 - other possible operations and sealing of the first and second support along their perimeter.
18. A process for the use of cesium dispensers according to claim 16, comprising the following series of operations:
- production of the first set of electrodes on the first transparent support;
 - production of the organic multilayer on the first set of electrodes;
 - production of the second set of electrodes on the organic multilayer;
 - evaporation of cesium on the second set of electrodes;
 - other possible operations and sealing of the first and second support along their perimeter.
-



BEST AVAILABLE COPY

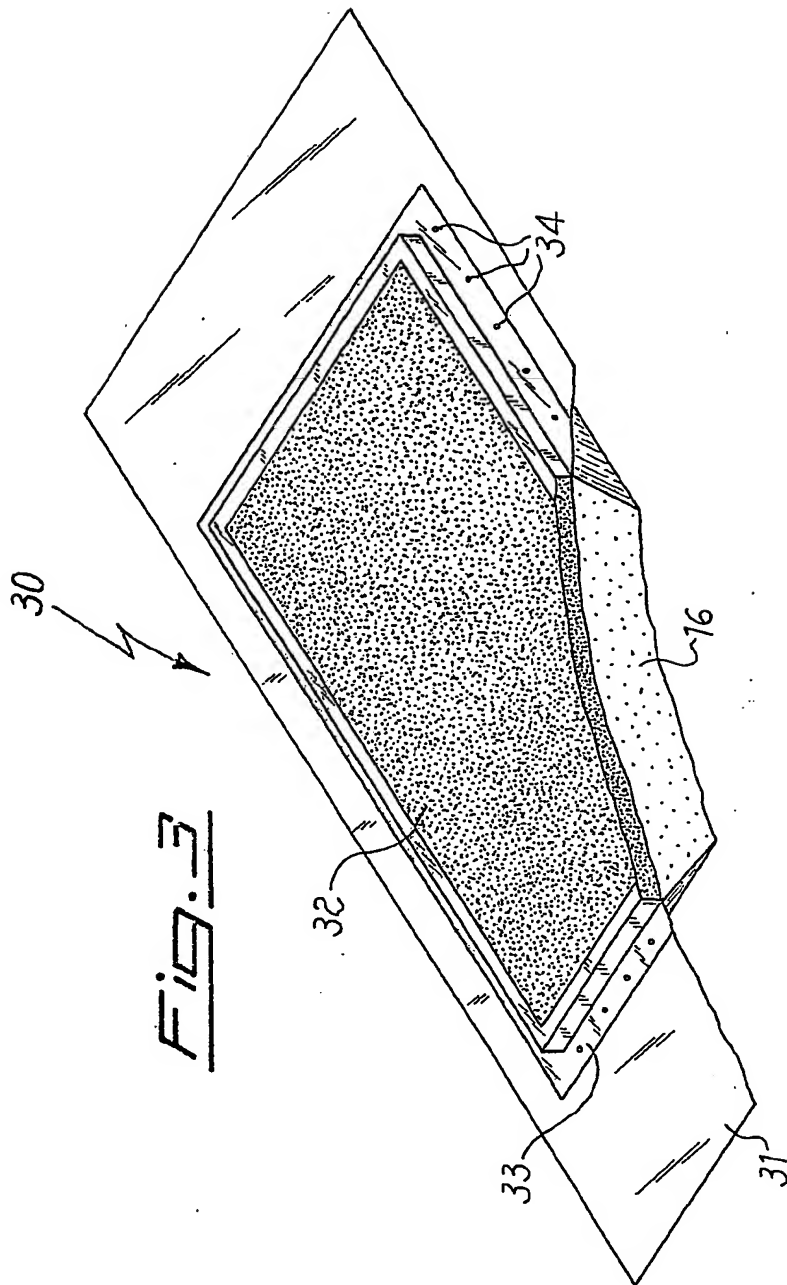
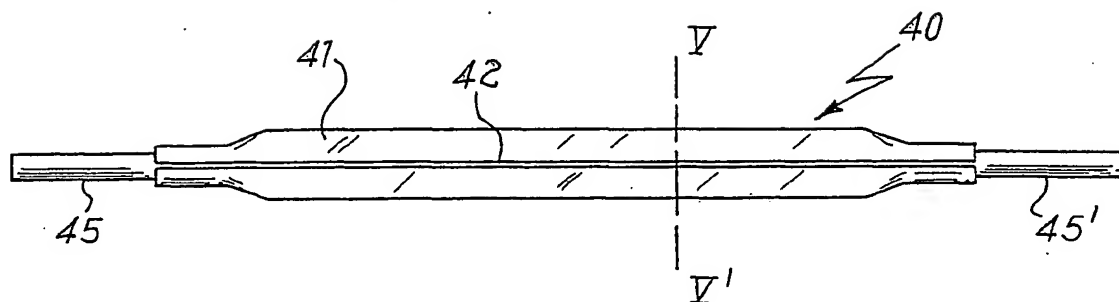


Fig. 4Fig. 5